

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (31-01-09)		2. REPORT TYPE FINAL		3. DATES COVERED (03-15-05 to 11-30-08)	
4. TITLE AND SUBTITLE Aluminum Cluster-Based Materials for Propulsion and Other Applications				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-05-1-0186	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Shiv N. KHANNA				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Virginia Commonwealth University 737 N 5 <sup>th</sup> St. RICHMOND VA 23219-1415				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF, AFRL DUNS 143574726, AF OFFICE OF SCIENTIFIC RESEARCH, 875 N. Randolph St., Room 3112, Arlington, VA 22203, JOYCE A. BURCH (703) 696-9729				10. SPONSOR/MONITOR'S ACRONYM(S) Br. Dr. Michael R. Berman	
				11. SPONSOR/MONITOR'S REPORT NUMBER AFRL-OSR-VA-TR-2013-1030	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The key objective of our work has been to study the interaction of aluminum and aluminum based clusters with organic templates, with oxygen and water, and develop protocols that would enable the synthesis of cluster assembled materials based on reactive and non-reactive motifs. Our studies on the reactivity of aluminum clusters with propene showed that the reactivity was related to the location of the unoccupied molecular orbital and that clusters like $Al_{12}^-$ , $Al_{15}^-$ , $Al_{18}^-$ , and $Al_{21}^-$ can readily bind to propene and hence may be suitable building blocks to generate such materials. For $Al_{13}$ , a superhalogen superatom discovered by us, our studies showed that an ionic assembly composed of $Al_{13}$ and super-alkali $K_3O$ is stable and ideal to generate an ionic solid. Through synergistic efforts combining theoretical studies in my group and experiments in A. W. Castleman's (AWC) group at PSU, we identified $Al_4H_7^-$ as a very stable species that is resistant to oxygen and ideal building blocks for cluster materials. We also showed that the reactive aluminum clusters can be made less reactive by adding H atoms as it changes the spin state of the system. We also established general protocols for using the findings on free clusters to generate cluster assembled materials and in collaboration with experimental groups, synthesized a cluster solid of $As_7K_3$ species through a directed chemical synthesis. Recently, in a synergistic efforts combining experiments in AWC group at PSU, we have discovered an unusual size dependent reactivity of aluminum cluster anions with water, in that $Al_{16}^-$ , $Al_{17}^-$ , and $Al_{18}^-$ are found to produce hydrogen through processes linked to their geometries. The studies provide a new Approach to synthesize hydrogen from water, on demand, and have just been published in SCIENCE. We believe that these developments are important towards cluster based materials for propulsion and nanoelectronic applications.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

# **AFOSR PROGRESS REPORT**

## **Principal Investigator:**

**S. N. Khanna**  
**Department of Physics**  
**Virginia Commonwealth University**  
**1020 West Main Street**  
**Richmond, VA 23284-2000**  
**Tel: (804) 828-1820**  
**Fax: (804) 828-7073**

## **Research Title:**

***Aluminum Cluster-Based Materials for Propulsion and other Applications***

**Grant No: FA9550-05-1-0186**

**Period of Performance:            March 15, 2005 – August 31, 2005**

## **Authorized VCU Representative:**

Susan E. Robb, CRA, Director  
Office of Sponsored Programs  
Virginia Commonwealth University  
P. O. Box 980568  
Richmond, Va. 23298-0568  
Tel: (804) 828-6772  
Fax: (804) 828-2521

**Objective:**

The key objective of the program is to carry out theoretical investigations of the geometries, stability, electronic structure and reactivity of aluminum based clusters and to explore the possibility of making materials using pure aluminum and compound aluminum based clusters as the building blocks. Previous studies have indicated  $\text{Al}_{13}^-$  as a very stable cluster with superhalogen attributes. Initial investigations will therefore focus on the possibility of materials using  $\text{Al}_{13}^-$  as a possible motif.

The proposed work is a synergistic effort combining the theoretical work at VCU and the experimental investigations in Prof. Castleman's group at Pennsylvania State University and in Prof. Bowen's group at Johns Hopkins University.

**Status of the Effort:**

This report covers the period beginning March 16, 2005 to August 31, 2005. During the first five months of the research project, we have embarked on three projects. (1) **Possibility of cluster materials using molecular templates.** Here, in a synergistic effort with Prof. A. W. Castleman, Jr., the interaction of aluminum clusters with propyne was undertaken to identify the factors governing the binding of clusters to organic templates. These investigations have just been accepted for publication in Chem. Phys. Letters. (2) **Possibility of composite units by combining  $\text{Al}_{13}$  with molecular units having low ionization potential.** Such combinations offer the possibility of forming ionic solids based on molecular units. We already have some preliminary promising results on a unit formed from  $\text{Al}_{13}$  and  $\text{K}_3\text{O}$  clusters. (3) **Identification of new aluminum based motifs that could serve as the building blocks.** The effort here is

directed towards developing principles that could guide the search of stable motifs called “superatoms”. A manuscript containing the results of these investigations is being prepared.

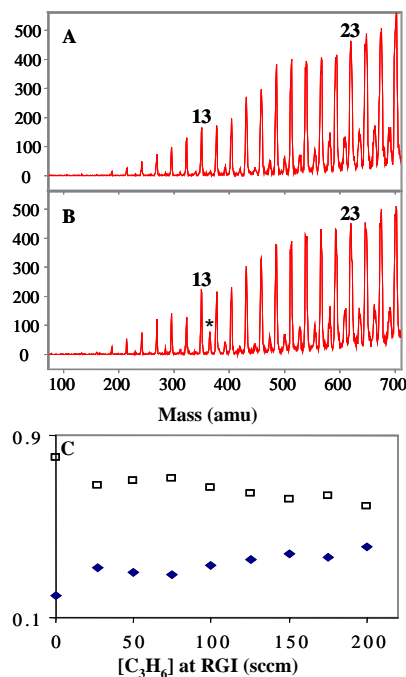
### Accomplishments/New Findings:

#### (1) Interaction of Aluminum Clusters with Organic Templates:

One of the approaches envisioned to form cluster based materials is to deposit clusters of interest on organic and inorganic templates. An understanding of the factors governing the interaction between aluminum clusters and templates is vital to translating this possibility into practice. As a first step towards this understanding, the reaction between  $\text{Al}_n^-$  and propene, which we adopt as a model alkene system, were carried out. We believe that these investigations also extend our previous base of knowledge about the reactivity of aluminum clusters as pertaining to organic species.

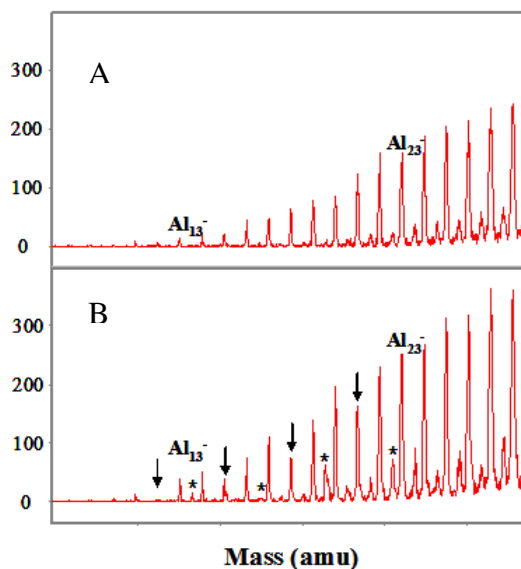
The experimental part of the program was carried out in the fast-flow tube apparatus in the laboratory of Prof. A. W. Castleman. In brief, clusters were generated via

**Figure 1.** Mass spectra of (A)  $\text{Al}_n^-$  clusters (B) reacted with 200 sccm of propene. The asterisk marks the  $\text{Al}_{12}\text{C}_3\text{H}_6^-$  peak. The branching ratio (C) shows the contribution of  $\text{Al}_{12}^-$  (open squares) and  $\text{Al}_{12}\text{C}_3\text{H}_6^-$  (closed diamonds) to the sum total of both species' ion signal as a function of increasing  $\text{C}_3\text{H}_6$  concentration.



vaporization of an Al rod in the constant flow laser vaporization source and subsequently reacted with propene. Collisions with the carrier gas cooled the clusters prior to reaction with propene. Figure 1 shows the results of these investigations. It was found that at moderate concentrations of propene, only one  $\text{Al}_n^-$  cluster,  $\text{Al}_{12}^-$ , undergoes a reaction. Figure 1C confirms the formation of an association product,  $\text{Al}_{12}\text{C}_3\text{H}_6^-$ . In Figure 2B, we show that several other clusters belonging to the series  $\text{Al}_{12+3n}^-$  (where  $n = 0, 1, 2$ , and  $3$ ) react with propene at higher concentrations, and in each case (with the possible exception of  $\text{Al}_{15}^-$ ) it seems that an association product is formed.

**Figure 2** Mass spectra of (A)  $\text{Al}_n^-$  clusters (B) subjected to a large dose of propene, the arrows point to the disappearing peaks that correspond to the  $\text{Al}_{12+3n}^-$  ( $n = 0 - 3$ ); asterisks mark the  $\text{Al}_{12+3n}\text{C}_3\text{H}_6^-$  adducts.

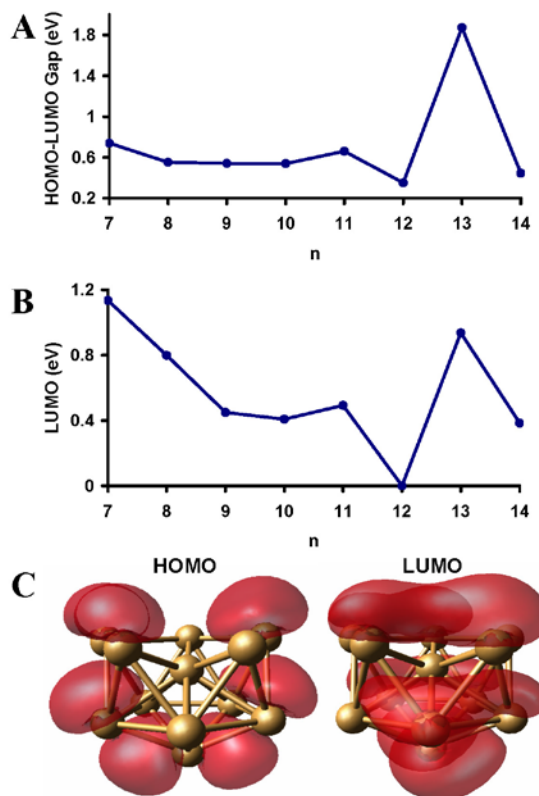


These experiments raised the question as to why  $\text{Al}_{12}^-$  is so reactive and what is the origin of the enhanced reactivity of  $\text{Al}_{12+3n}^-$  (where  $n = 0, 1, 2$ , and  $3$ ) at higher concentrations.

To understand these results, ab-initio calculations of the structure of pure and reacted aluminum clusters were carried out. Previous investigations by Chrétien *et al.*<sup>1</sup> on reactions of propene to  $\text{Ag}_n$  and  $\text{Au}_n$  clusters had suggested that propene binds by donating charge from its HOMO to the metal cluster and that the binding is stronger

when the LUMO of the metal cluster is lower in energy as it facilitates the charge transfer. Further, propene binds preferentially to the site on the cluster where a lowest unoccupied molecular orbital (LUMO) protrudes most into vacuum. We find similar effects in aluminum clusters. In Figure 3, we show the HOMO-LUMO gap and the position of the LUMO relative to that in  $\text{Al}_{12}^-$  in clusters containing 7-14 atoms. Also shown are the charge densities of the HOMO and LUMO. Note that the  $\text{Al}_{12}^-$  has the lowest HOMO-LUMO gap and is expected to be reactive. However, one further notices that the actual energy of

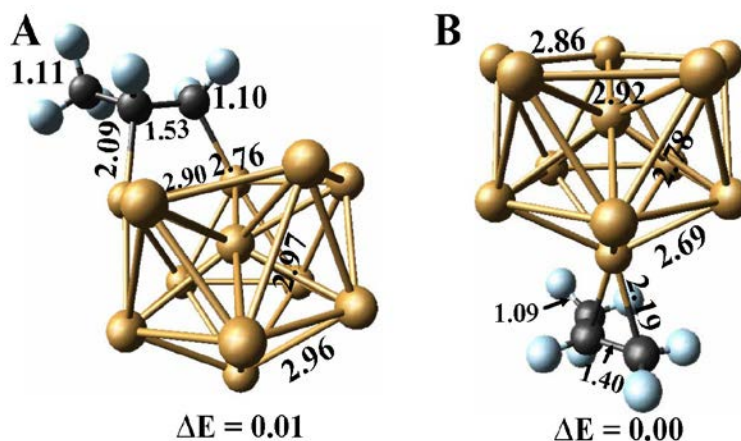
**Figure 3** (A) Plot of the HOMO-LUMO gap as a function of cluster size in the series  $\text{Al}_n^-$ . (B) Plot of the energy of the LUMO as a function of cluster size in the series  $\text{Al}_n^-$ . The energy is set relative to the LUMO energy for  $\text{Al}_{12}^-$ , which is shown here as zero. (C) Lowest energy structure and maps of the charge density for the HOMO (left) and LUMO (right) of  $\text{Al}_{12}^-$ .



the LUMO is also anomalously low. The plot of the charge density of the LUMO of  $\text{Al}_{12}^-$  (Figure 3) shows a protruding lobe at the face-capping apical site mentioned above. Figure 4B shows that association of the  $\text{C}_3\text{H}_6$  cluster to this site resulted in the ground state cluster. In addition, a large protruding lobe can be found above the uncapped

pentagonal Al ring. Propene association to this site of  $\text{Al}_{12}^-$  shown in Figure 4A is found to be an isomer of the cluster shown in Figure 4B. Either of these

**Figure 4** (A) Geometry of a low lying isomer of  $\text{C}_3\text{H}_6$  associated with  $\text{Al}_{12}^-$  and (B) the ground state structure.



lobes should provide the charge accepting behavior necessary for favorable adsorption of propene.

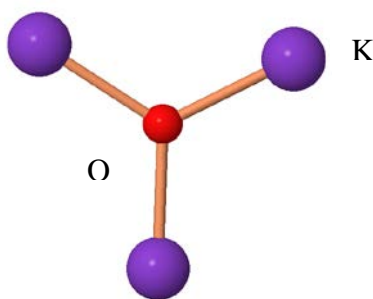
As mentioned above, at higher concentration of propene,  $\text{Al}_{15}^-$ ,  $\text{Al}_{18}^-$ , and  $\text{Al}_{21}^-$  also react with propene. The  $\text{Al}_{13}$  cluster has a complete geometric shell around a central atom. The ground state of the anion is a perfect icosahedral structure that has a  $\text{C}_{3v}$  symmetry and can be described by two sets of two triangles each around the central site. The triangles closer to the central site have larger bond lengths while the triangles away from the site have smaller bond-lengths. One could grow the icosahedra by adding 3 atoms at a time leading to  $\text{Al}_{16}^-$ ,  $\text{Al}_{19}^-$  and  $\text{Al}_{22}^-$  species corresponding to partially filled geometric sub-shells. One could therefore regard  $\text{Al}_{15}^-$ ,  $\text{Al}_{18}^-$ , and  $\text{Al}_{21}^-$  as incomplete geometric shells like  $\text{Al}_{12}^-$  and hence more reactive. These investigations are currently being pursued. In the same vein, it will also be important to extend the present investigations to address the reactivity of activated  $\text{Al}_n\text{I}_x^-$  clusters towards propene. Present knowledge of  $\text{Al}_n\text{I}_x^-$  clusters allows the prediction that propene will bind selectively to species with active centers (those with odd  $x$ ). Based on the reactivity

studies and the calculations that showed preferential attachment of additional I atoms to these sites, it is reasonable to assume that the lobes mapped for the HOMO levels in active  $\text{Al}_n\text{I}_x^-$  clusters will provide the electronic equivalent of the protruding LUMO's. If such reactions are shown to be possible with halogen-like superatom clusters<sup>2-4</sup>, an exciting step towards new synthetic chemistry would be realized.

## (2) Ionically Bonded $\text{Al}_{13}\text{M}$ Systems using Molecular (M) Cations:

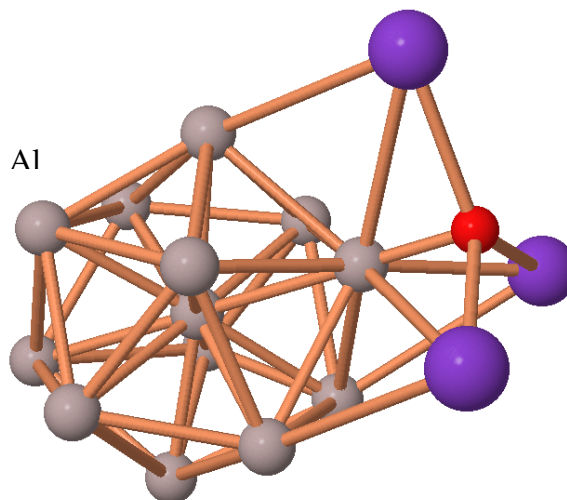
As Previous stated, an  $\text{Al}_{13}^-$  cluster has an electron affinity comparable to that of an halogen atom and hence it should be possible to form ionic compounds by combining  $\text{Al}_{13}$  with alkali atoms. Previous studies in our group on  $\text{Al}_{13}\text{K}$  indeed showed it to be an ionically bonded molecule composed of  $\text{Al}_{13}^-$  and  $\text{K}^+$  units much like the ionic salt  $\text{KCl}$ . Since the size of K is much smaller than that of  $\text{Al}_{13}$ , attempts at forming materials by assembling  $\text{Al}_{13}\text{K}$  units resulted in strong interactions between the  $\text{Al}_{13}$  motifs resulting in the fusion of the clusters. One way to overcome this obstacle is to use larger molecular units with lower ionization potentials as cations. The first such unit that we are trying is  $\text{K}_3\text{O}$ . It has a planar structure shown below.

Fig. 5. Ground state geometry of  $\text{K}_3\text{O}$ .



Our studies indicate that it has an ionization potential of 3.25 eV which is much lower than that of even K. Using such a motif, initial calculations of the binding of  $\text{K}_3\text{O}$  to  $\text{Al}_{13}$  were performed. The following figure shows the final ground state geometry of

Fig. 6. Ground state geometry of  $\text{Al}_{13}\text{K}_3\text{O}$ .



the complex. Interestingly, the geometry of the  $\text{Al}_{13}$  cluster is very similar to that of  $\text{Al}_{13}^-$  indicative of some sort of ionic bond. The complex has a large binding energy of 5.65 eV (with respect to isolated  $\text{Al}_{13}$  and  $\text{K}_3\text{O}$ ). The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 1.22 eV. The large binding and a substantial HOMO-LUMO gap are both indicative of the very stable nature. How do such units bond?

The next investigations focused on a dimer composed of  $\text{Al}_{13}\text{K}_3\text{O}$  units. The two units were placed in several orientations and the energy minimized by moving atoms in the direction of forces till the forces became less than a critical value. The following figure shows the lowest energy structure.

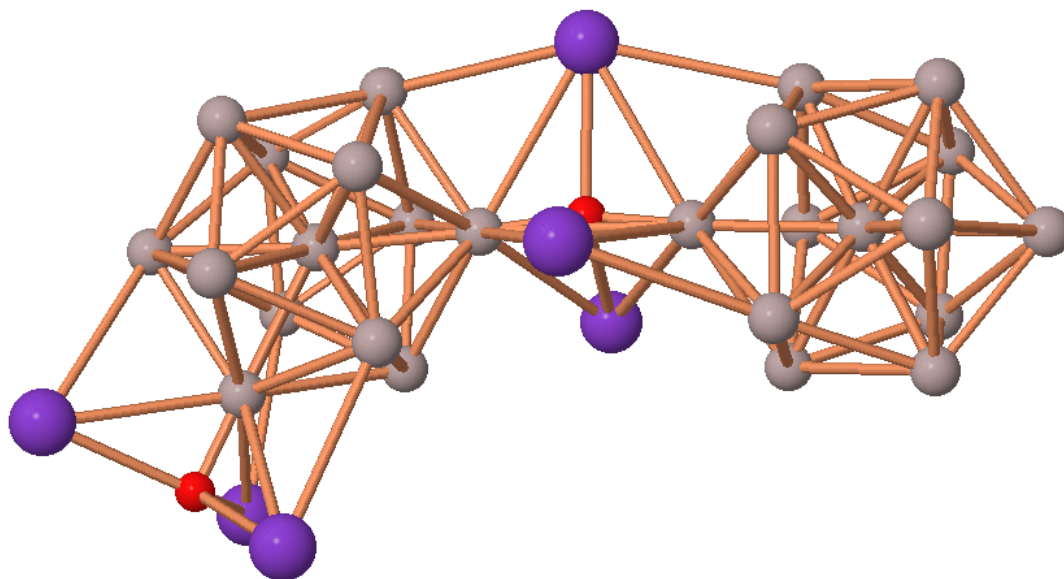


Fig. 7. The ground state geometry of  $(\text{Al}_{13}\text{K}_3\text{O})_2$  cluster.

Note that the  $\text{Al}_{13}$  units maintain their identity providing optimism that one may be able to form cluster materials. We are in the process of exploring this possibility by extending these studies to bigger systems.

### (3) Identification of New Superatoms:

In a synergistic effort combining experimental work in the group of Prof. Castleman and the theoretical investigations in our group, we had previously demonstrated that  $\text{Al}_{13}^-$  behaves like a halogen while  $\text{Al}_{14}^{++}$  behaves like an alkaline earth.

As the electronic, magnetic, optical or chemical properties in clusters are controlled by geometrical shape, size, and composition, the use of superatoms offers the possibility of forming materials with desirable collective traits using selected species. Our effort is now directed towards finding more members of the “superatom” family.

We have just demonstrated a new member of the superatom family, namely  $\text{Al}_7$ . What is truly remarkable is that unlike previous members, this new member exhibits

multiple valence states in close analogy to non-unique valence states exhibited by several atoms. An important outcome of the multiple valence is the ability of the superatom to form stable compound clusters when combined with different atoms. In particular, one can not only understand the stability of  $\text{Al}_7\text{C}^-$  and  $\text{Al}_7\text{N}^-$  reported in previous mass spectra, but one can also predict stability of numerous other species namely  $\text{Al}_7\text{O}^-$ ,  $\text{Al}_7\text{O}_2^-$ ,  $\text{Al}_7\text{Cl}$  and  $\text{Al}_7\text{Cl}_3$ . These are exciting developments and are currently being pursued.

#### References:

1. Chrétien, S.; Gordon, M.S.; Metiu, H. *J. Chem. Phys.* **2004**, 121, 3756 ; Chrétien, S.; Gordon, M.S.; Metiu, H. *J. Chem. Phys.* **2004**, 121, 9925.
2. Bergeron, D.E.; Castleman, A.W., Jr.; Morisato, T.; Khanna, S.N.; *Science* **2004**, 304, 84.
3. Bergeron, D.E.; Castleman, A.W., Jr.; Jones, N.O.; and Khanna, S.N. *J. Chem. Phys.* **2004**, 121, 10456.
4. Bergeron, D.E.; Roach, P.J.; Castleman, A.W., Jr.; Jones, N.O.; Khanna, S.N. *Science* **2005**, 307, 231

#### Personnel Supported:

S. N. Khanna (1 summer months), Principal Investigator

J. Ulises Reveles (Post Doctoral associate, will be supported starting November).

#### Publications:

1. Bergeron, D. E., Castleman, A. W., Jr., Jones, N. O., and Khanna, S. N., *Chem. Phys. Lett.* (in Press).

2. Ulises Reveles, J., Khanna, S. N., Castleman, Jr., :Multiple Valence Superatoms (Being Prepared).

**Interactions/Transitions:**

(a) *Participation/presentation at meetings, conferences, seminars, etc.*

1. US Army Research Laboratory at Aberdeen Proving Ground, Maryland, April, 2005.
2. Collegiate High School, May 2005.
3. AFOSR Contractors Meeting on Molecular Dynamics/Theoretical Chemistry May, 2005
4. XIV International Materials Research Congress”, Cancun, Mexico- Aug. 2005.
5. American Chemical Society Meeting, Washington, Aug. 2005.
6. International Chemical Congress of Pacific Basin Societies, Hawaii, 2005.

(b) *Consultative and Advisory Functions.*

(c) *Transitions.*

**Discoveries/Inventions/Patent Disclosures.**

Our finding that Al13 has properties like halogen atoms and Al14 has behaviors reminiscent of alkaline earth atoms has been covered by more than 50 news agencies around the world.



Honors/Awards: None